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Coherent Motion of Excited State Cyclic Ketones: The Have and the Have-Nots[†]

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Abstract

The internal conversion processes of four cyclic ketones; cyclopentanone, 2-methylcyclopentanone, 3-methylcyclopentanone and cyclohexanone are investigated by Velocity Map Imaging (VMI) photoelectron spectroscopy. A 201 nm pump accesses the second excited state ($n,3s$) and the ultrafast dynamics is mapped by subsequent ionization with a 350 nm probe. Three of the four investigated molecular systems show an oscillatory time-dependence in the peak position of the $3s$ photoelectron band, while the last one simply decays exponentially. We find that the most plausible reason for the absence of the oscillation is due to high structural similarity between the excited state and the ionic state along the active coordinate.

1. Introduction

The first report of picosecond molecular coherences by Zewail and co-workers [1] initiated an era of investigations of ultrafast molecular dynamics. One example is the investigation of the nature of the diradical involved in the ring-opening and decarbonylation of cyclic ketones [2], a contribution which was also noted by the Nobel committee [3]. The ability to follow a chemical reaction across the transition state highlights the unique capabilities of the femtosecond technique in chemistry [2] although no coherent motions were observed in this specific case. Cyclic ketones are also the subject of investigation here but with a narrower focus on the possible coherences in the non-radiative transition between electronic states.

The early reports on the photochemistry of vapour phase cyclic ketones include the studies of Norrish and co-workers [4] and marked a starting point for using ever more differential experiments and increasingly detailed theory to understand the fundamental photophysical processes of the carbonyl chromophore. The solution phase chemistry of cyclic ketones merits mention as an important complimentary experiment acknowledged early on [5] and the photochemical reactivity in solution [6–8] provided much information on the photophysical processes occurring from the lowest excited singlet state. Investigations into the VUV spectrum and Rydberg states have been done by resonance enhanced multiphoton ionization (REMPI) methods [9–13], electron ionization [14] and absorption [15–19]. In the gasphase the first excited state absorption of cyclic ketones occur around 4.1–4.4 eV and has (n,π^*) character. The second and higher energy excited states have Rydberg character, starting with the ($n,3s$) state which absorbs around 6.2 eV and the $3p$ Rydberg states follow ~ 0.7 eV above the ($n,3s$) absorption.

Zewail and his co-workers expanded the studies of cyclic ketones by time-resolved mass spectrometry experiments [2,20–24] and focused on identifying transition states between highly excited electronic states. The studies showed the non-ergodicity of ultrafast relaxation processes

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